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Kinetic Aspects of Flame Inhibition by Halons and Halon Alternative Compounds

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Introduction

Current interest in replacements for Halon 1301(CF₃Br) has opened once again the issue of the physico-chemical basis for fire suppression. This paper is intended to provide information necessary for understanding the quantitative aspect of the chemistry of the process and to suggest how such knowledge may further understanding of the phenomena. The direct aim is to set the stage for the extensive simulations that will be carried out in the near future. With current and developing knowledge on the fundamental chemical kinetic processes many of the uncertainties on this issue can be considerably reduced. The consequence is that some of the older questions may be settled, and the power of empirical tests enhanced. This can lead to an improved capability for the selection of an appropriate substitute not only for ozone depletion but also in the context of global warming or a particular combustion threat. This is the rationale and promise of more fundamentally based approach implicit in chemical kinetic simulations. Specifically, environmental concerns have added extra dimensions to the traditional chemical optimization problem. Testing requirements are vastly increased. In the present case, a solution to the ozone depletion problem may well be deleterious from the point of view of global warming. At the same time greater understanding also offers the possibility of a more appropriate match of solution to threat.

This paper will be divided into four parts. Following this introduction, we give background material on a number of the issues pertinent to this discussion. The principal part of this paper will cover the chemical kinetics aspects of combustion and suppression through a description of the quantitative data that now exists and that have been used in other contexts. The section will contain discussions on the most obvious gaps in understanding. We conclude with general comments on a variety of ancillary issues that arise from the present approach.

Background

A comprehensive review on possible substitutes for halons was published in 1990. The paper also contains background information on experimental observations and the current state of understanding of the flame suppression phenomenon¹. For the present purposes, it is important to remember that there are a wide number of tests that can be

used to classify compounds in terms of their efficiency as a fire suppressant. The meaning of such tests in terms of the fundamental chemical changes are however unclear. In all of these tests Halon 1301 has always ranked very high. Since it is extraordinarily non-toxic, until the advent of the ozone depletion problem, there has been no necessity for any deeper understanding of its fire suppression capability and therefore very little research has been carried out. Furthermore, for many years the tools were not available to make decisions on the various alternative mechanistic possibilities. The long standing controversy over the relative importance of physical versus chemical effects in fire extinguishment could not really be settled without a quantitative understanding of the chemical processes in question. The simulations that is currently being carried out should answer such questions definitively. Furthermore, the studies can have the important effect of permitting finer control with regard to the response to a particular fire situation. This is especially important since one cannot expect any new fire suppressant to have the identical properties of Halon 1301 and similar compounds that are to be replaced.

Intrinsic to understanding fire suppression is a proper description of the underlying combustion process. The general mechanism of how and why hydrocarbons burn has been understood for many years². Summarizing briefly, the overall reaction involves small reactive radicals such as OH, H, O, etc which rapidly destroy fuel molecules and in the process create more radicals of the same type. The destruction process is then started all over again. Since the general trend is towards greater degrees of oxidation, thermodynamics dictate that the temperature of the mixture rapidly increases. Thus, the exponential dependence of rate processes on temperature means that the reaction is accelerated and even more radicals are produced. The consequence is extremely rapid consumption of the fuel and conversion to CO₂ and H₂O.

Obviously, anything that intercepts the radicals and prevents them from reacting further or lowers the temperature and thus slow down the rate of chemical reaction will have a deleterious effect on combustion. Note that this description encompasses both physical and chemical causes for flame suppression and one can invoke scenarios where one or the other becomes predominant. Such qualitative understanding cannot however be directly used. What is needed is quantitative information that defines the various parameters necessary for characterizing a fire situation. Clearly, both physical and chemical kinetics must be considered. This is a technically challenging task. This discussion will be focussed about the chemical aspects of the phenomena and represents a serious simplification of the problem. However, for the present application, one does not seek absolute answers. Instead, comparisons are being made regarding the relative behavior of various compounds. Thus, it should be possible to cover all potential chemical situations and in certain cases draw appropriate conclusions.

Although gas phase chemical kinetics has been studied for over half a century, it has only been in the last few years that the accumulation of higher temperature thermal rate data has led to sufficient critical mass so that detailed computer simulations based on elementary thermal rate data is meaningful. Of course, an equally important prerequisite for carrying out such simulations is the power of modern computer technology in terms of modern hardware and software. Such progress can be expected to continue. Thus, what are serious computational problems today can be expected to be of much less consequence in the near future. Indeed, it is likely that the main bottleneck to the

exploitation of the technology is the availability of high quality chemical kinetic information. Even with what is available, a variety of well known combustion phenomena such as knock, autoignition, soot formation^{3,4} can be reproduced from simulation studies.

Westbrook⁵ has carried out an important study on the effect of 1301 and other brominated compounds on a variety of light organic flames. He was able to match experimental observations of various species determined from mass spectrometric sampling of low pressure flames and demonstrated that the principal inhibitory mechanism was the removal of hydrogen via the reactions $H + HBr = H_2 + Br$; $H + Br_2 = HBr + Br$; and $Br + Br + M = Br_2 + M$ leading to the overall process $H + H = H_2$. The principal role of the fluorine was apparently to absorb hydrogen atoms in the form of HF and thus remove them from the radical pool. The general trends are what one would expect and support contributions of chemistry to flame inhibition. However, as pointed out by Westbrook, there are considerable uncertainties in the kinetics that is used in the modelling. This becomes particularly serious when one wishes to compare the inhibitive properties of various compounds. In these cases uncertainties in rate constants may become very important. It is somewhat unfortunate that the work of Westbrook was carried out just when systematic collection and evaluation of kinetic data bearing on general combustion issues began⁶. The subsequent section of the paper will cover this issue. Summarizing, there have now been a number of simulation studies that reproduce well known combustion phenomena at least at the semi-quantitative level. What has not been done is to use simulation in the predictive mode. The present simulation efforts on halon substitutes can thus be considered among the first of what will inevitably become a standard means of dealing with chemical problems related to combustion phenomena.

Chemical Kinetic Data Base

The fundamental processes that govern gas phase chemical change during combustion are single step thermal reactions. They involve reactions of molecules with Boltzmann averaged distributions and occur as written. The rate constants for these reactions are the first transferrable bit of kinetic information for such processes. This is in contrast to rate constants for global reactions. For example, while it is possible to derive the rate constant for the conversion of hydrocarbons to water and carbon dioxide in the presence of oxygen, such a number is system specific. Therefore it has no predictive capabilities except for similar systems. The more fundamental approach can lead to predictions subject to the accuracy of the rate constants that are used as input data. The practical disadvantage is the large amount of data that is needed. As noted earlier, this problem is being gradually solved. A particular advantage of the more fundamental approach is that theory can be used for interpolations, extrapolations and increasingly predictions. Thus a limited number of accurate rate constant measurements can be leveraged into prediction for that of other reactions. Thus there is no particular necessity for determining every rate expression at the conditions desired. In the following paragraphs the present situation with respect to the kinetic data base for hydrocarbon combustion will be reviewed.

The potential of chemical simulation has led to systematic attempts at chemical kinetic data base development. These first began to appear in the mid-1970s. It should be emphasized that for any particular system, the overall process can probably be described by the rate expressions for a few main reactions. However, different processes require

different main reactions and they can only be determined after all possibilities have been considered. Thus a proper starting point is probably to consider all possible reactions. This is the approach taken by the effort at the National Institute of Standards and Technology for hydrocarbon combustion^{7,8}. The procedure is to begin by listing all species, stable as well as unstable, that can be present in a particular combustion system and then considering all possible interactions between these species. In the context of thermal reactions for C/H/O systems only unimolecular and bimolecular processes need to be considered. Reactions in the intermediate pressure range (unimolecular and bimolecular and bimolecular and termolecular) can be treated using the very successful RRKM theory⁹ using as a basis the limiting rate high and low pressure rate expressions.

In the construction of the data base, the basic procedure is to examine the existing measurements, carry out the best possible evaluation and give a recommendation along with the estimated uncertainties. Where data does not exist a best possible estimate is made. The theoretical basis for estimates and evaluations are detailed balance, the constraints set by thermodynamics and the precepts of thermochemical kinetics which is essentially a set of semi-empirical rules built upon existing data and with a basis in transition state theory and the group properties of organic molecules. For small organic molecules there are large volumes of experimental measurements. Furthermore, practically all the reactions involve simple bond breaking or formation. It is therefore possible to make good estimates. The approach outlined here has proved to be quite successful and productive. Figure 1 represents a summary of the present status of the NIST program^{7,8}. The results are presented in the form of a reaction grid and each cross represent an interaction for which recommendations are given. These can of course lead to a variety of products. Thus the actual number of reactions considered are considerably larger than the number of crosses. The unmarked squares represent interactions which do not result in reaction. The advantage of this systematic approach is that there is no possibility that an important reaction process will be inadvertently left out for the simulation.

It should be emphasized that the NIST effort is not unique. Warnatz¹⁰ has also published listings of recommended rate expressions. A collective effort by kineticists from the European Community has also been published¹¹ recently. Since chemical kinetics is an active research area with new measurements and theories being steadily produced, the latest evaluation should be preferred. The NIST publications are probably the most complete and therefore an important starting point. The situation with respect to the chemical kinetic data base for the combustion of small organics is fairly satisfactory in the sense that most modeler should be able to readily access the available kinetic data.

These can also be used as a basis for the estimation of the rate constants for the combustion of more realistic fuels. There are, however, certain problems associated with new reaction pathways, such as concerted molecular processes and radical isomerization reactions, which remain to be assessed if predictions from such simulations are to be used with the same confidence as that for smaller molecules. An additional lack of the existing data bases are the reactions leading to aromatics and soot formation. For many situations these reactions may not be very important in flame suppression. The possibilities nevertheless should be examined. Frenklach and coworkers⁴ have developed models for soot formation. Thus users must in general depend on the primary literature.

For flame suppression, it is necessary to integrate into the existing data base information on the reactions of the compounds in question. Westbrook has done this for CF_3Br and this is an appropriate beginning. It is necessary to point out that although the intention is to find substitutes for this compound, if simulations are to be used as a predictive tool, it is absolutely essential that initial work begin here since what is wanted is a comparison between the suppression propensities of various compounds. Without simulations using Halon 1301, one has no basis for comparison. There are extensive tests that point to the fire suppression superiority of CF_3Br in comparison to other compounds. A key tests of the validation of the simulation results is the correspondence with test data. When this can be demonstrated one can then confidently extend the simulations to cover situations and compounds that have not been tested.

The work of Westbrook on CF_3Br contains a set of 56 reactions which he integrated into his data base for the combustion of a number of small hydrocarbons. This is a natural starting point for further work. Unfortunately, since the data base used in the work was first collected there have been considerable changes in the rate expressions that should be used for such simulations. Some of the changes are summarized in Figure 2^{6,12-14}. It can be seen that these can be as large as an order of magnitude and are quite basic to the extinguishment mechanism. In addition there are changes in mechanism that must be accommodated. For example the interaction of $\text{CF}_3 + \text{O}_2$ is alleged to proceed to $\text{CF}_2\text{O} + \text{OF}$. This is undoubtedly based on the comparable process with methyl. It is now generally agreed that this interpretation for methyl radical reaction with O_2 is in error and in any case fluorine is known to be much less subject to internal migration. The proper reaction is $\text{CF}_3 + \text{O}_2 = \text{CF}_3\text{O} + \text{O}$. An added benefit of such a process is that since it involves straightforward bond breaking and forming through the formation of an intermediate complex, RRKM calculations can in fact yield rate constants. Furthermore, if the reaction postulated by Westbrook is unimportant it is then possible to eliminate the species FO from consideration. The elimination of any species has the important effect of removing all reactions involving that species from the data base. This can lead to drastic simplification of the mechanism. On this basis it is clear that the earlier work of Westbrook must be redone with a more valid data base. Work in this direction, paying particular attention to fluorine type chemistry is being carried out at NIST.

Overall, there exists considerable data upon which one can base simulation studies. The previous work by Westbrook is extremely encouraging in the sense that he was able to demonstrate that chemical effects do effect flame properties. There is obvious need to tighten up the uncertainty limits of a large number of the rate expressions that are used. Some of the thermodynamic properties used by Westbrook should probably also be upgraded. Here, developments in computational chemistry can have very important consequences. In addition, it is uncertain whether the 56 reactions listed by Westbrook exhaust all the possibilities. We prefer the more systematic approach of considering all reactions initially and then reducing them on the basis of sensitivity analysis.

Special Issues

More recently, it had been noted that the presence of compounds such as HCl ¹⁵ in incineration systems can have severe effects in reducing steady state OH concentration through the reaction $\text{OH} + \text{HCl} = \text{H}_2\text{O} + \text{Cl}$. The consequence is that the final heat release

process $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$ is retarded. One would expect that this may have an important inhibiting effect. Such a reaction can also have consequences for HBr. On the other hand, HI, with its lower bond energy would be present in much smaller amounts as the temperature is increased. OH will therefore not be scavenged. Similarly, note the requirement for Br_2 for the catalytic cycle given above. However if the temperature is sufficiently high then decomposition will predominate and the catalytic cycle will not be in effect.

Overall, chemical mechanisms for suppression makes temperature a very important variable. The thermal stability of the suppressant is another property of considerable consequence. Obviously, a compound that does not decompose in combustion situations can only exert a physical effect. The order of bond strengths for the various halides are $\text{C-F} > \text{C-Cl} > \text{C-Br} > \text{C-I}$. Aside from unimolecular decomposition the only way by which radical can be released into the system is through abstraction of the halide. For electronegative radicals such as O and OH, thermochemistry makes reaction probability with perhalogenated compounds small. The most likely process is attack by hydrogen atoms. However the data on hydrogen abstraction of fluorine is highly uncertain. We are currently carrying out studies on this question. This is especially important for the completely perfluorinated compound. Their great thermal stability if coupled with a slow rate constant for H attack means that radical will not be released into the system until much higher temperatures. This in turn means that chemical effects from suppressant activity cannot express themselves until much higher temperature than the other halides.

The differences between the thermal stability of the suppressant and that of the fuel and its reactivity with oxidant is another factor that should be considered. Note that for the type of chemical mechanism proposed by Westbrook halogen atoms must be released into the system. However initially they can also initiate decomposition and begin the combustion process. Thus fire suppression from a chemical point of view probably involves a subtle interaction of a number of processes. Definitive results cannot be obtained without detailed modeling.

The above discussion makes clear that chemical kinetic modeling of fire suppression is essentially another test method. It is presently at an early point of development. However the direction of technology is such that it inevitably will get better. Note that the ozone depletion problem is to a large extent a consequence of similar simulations. Even now, computation is far less expensive than many laboratory tests. Because it is anchored in the fundamentals the results are far easier to interpret. Furthermore, one can explore a whole range of fire scenarios. In the area of flame suppression chemistry it is particularly fortunate in that there exist from other contexts (from the development of chemical kinetic data bases for ozone depletion chemistry) much of the chemistry and of course a great deal of test data. Thus, the elements are in hand to develop the powerful technology for use in the near future by combustion scientists.

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Figure 1. Reaction grid for combustion of small organics from work at NIST, Ref(7). The species form the axis of the grid. Crosses represent reactions for which recommendations are given. Blanks imply reaction whose rate constants are too small to be of concern

[illegible]

Figure 2:
Comparison of
currently accepted
rate constants with
that used in
Westbrook Ref(5).
The names refer
to Ref(12), Russell;
Ref(13), Atkinson,
Ref(11), Baulch
and Ref(14) Seakins

